

Viet Nam National University – Ho Chi Minh City

University of Technology

HA LAC NGUYEN

**DESIGNED SYNTHESIS OF NOVEL METAL–ORGANIC
FRAMEWORKS FOR PHOTOCATALYST APPLICATION**

Doctorate Thesis – Summary

Advisors

Prof. Dr. NAM T. S. PHAN

Dr. DANH T. TONG

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ABSTRACT

Over the past two decades, the prominent growth of Metal Organic Frameworks (MOFs), a high ordered and porous material class had been receiving the pay attention by the research community specially. Constructing by Secondary Building Units (SBUs) of metal clusters and organic linkers combination permits the modification of resultant structural modularity for designing structure (e.g., post-synthetic modification, predesigned linker, defects chemistry) which can be tunable the structural features (e.g., pore size, porosity) to make MOFs address the environment problems as well as the targeted applications such as gas uptake, separation, catalyst, drug delivery, water treatment.

In MOF chemistry, the building block method, whereby discrete, preassembled metal oxo clusters are reacted with well-defined organic linkers, has been utilized to achieve a greater degree of control over MOF construction. However, the isolation and subsequent usage of many discrete metal oxo clusters remains a significant challenge and the relatively slow kinetics originating from the association and dissociation of ligands, limits the applicability of this method. Additionally, it is far from given that the desired MOF structure will be obtained as metal oxo building blocks have been observed to rearrange during the synthesis. Means of overcoming this lack of total synthetic control is to take inspiration from molecular synthesis, in which certain conditions have been discovered to achieve specific end products. In this contribution, we articulate a strategy for making discrete metal clusters *in situ* that are appropriately functionalized to affect imine condensation reactions, commonly used in the chemistry of covalent organic frameworks (COFs). We find that the cluster formation chemistry and that of COFs, when carried out in sequence, overcome the challenge of synthetic incompatibility. The structural

features of targeted material, termed MOF-901, was fully characterized powder X-ray diffraction and supplemental analyses. As a result of the incorporation of Ti(IV) units, MOF-901 was proven to be photocatalytically active and was applied to the photocatalyzed polymerization of methyl methacrylate (MMA).

For further investigation the photocatalysis properties of MOF which is isorecticular to MOF-901 structure, MOF-902 was successfully synthesized by enlarging the linking unit, and applied to the application of polymerization reaction with these kinds of monomer: methylmethacrylate (MMA), benzylmethacrylate (BMA), and styrene (St). Interestingly, based on the catalysis effect of MOF-902, the molecular weight of polyMMA is as high as the value of polyMMA which is produced by MOF-901 catalyst, and the polydispersity index of polyMMA produced by MOF-902 catalyst is lower than MOF-901 (1.27 compared to 1.60).

Moreover, we have successfully synthesized three novel MOFs termed MOF-903(Fe), MOF-904(Fe), and VNU-18(Cu) based triangular Iron (III) cluster and extraordinary three discrete Cu(II) building units, respectively. These materials were full characterized by the powder X-ray diffraction, single crystal X-ray diffraction analysis, thermogravimetric analysis, gas adsorption study. MOF-904 and VNU-18 show the permanent porosity with the internal surface area in calculated of $1200 \text{ m}^2 \text{ g}^{-1}$ and $1000 \text{ m}^2 \text{ g}^{-1}$, respectively, which are proven by Nitrogen isotherm at 77 K at low pressure.

CHAPTER 1. INTRODUCTION TO MOFs

1.1 Introduction

Metal Organic Frameworks (MOFs) are constructed by the rigid coordination bonds between the organic linkers and inorganic metal ions or clusters as the nodes which is widely designated by Secondary Building Units (SBUs) later. The organic linkers are also termed as SBUs in term of geometrical views as well. It is noted that MOFs have been termed as many names from the first time of invention (Porous Coordination Polymers (PCPs), Porous Coordination Networks (PCN), hybrid inorganic-organic materials, Metal Organic Materials (MOMs), etc.). Those names presented to the same general type of porous material which links two components of transition metals and organic linking units to form the extended structure. In fact, an early report in 1979 was published the cyanide-bridged mixed-metal open framework, in which the authors mentioned the similarities between their network and Zeolites. The outbreak of research in crystalline material based on metal ions and organic bridging ligands was continue in the late 1990's. The name of "Metal Organic Frameworks" has been become famous and popular by Omar M. Yaghi in 1995. More than 20,000 structures of MOFs have been reported and studied so far showing the tremendous development process of crystalline and porous materials. MOFs have been considered as the new class of microporous materials possessing the promising properties of high porosity, well-defined crystallinity, thermal stability, catalytic activity and so on. The key point of the structural features of MOFs in many cases as gas storage, separation, catalyst, drug delivery is determined by ultrahigh porosity and high internal surface area of MOFs. However, some certain applications: Proton conduction, magnetic behavior, catalyst, are related strictly to the active sites (metal cluster, linker active sites, exchanged counter ions) or post synthesis modification (PSM) to the structure of the host materials instead of high surface area of MOFs. In general, MOFs can be designed not only by employing the different metal coordination or diverse linker units but also by embedding a

specific environment to the void space inside the structure. The challenging in porous materials (Zeolites, activated carbon, etc.) is controlling the size, shape, functionality of the void space can be achieved in MOFs.

1.2 MOFs composites

MOFs are made from organic linkers and most of metals in periodic table from rare earth elements to *d*, *f*-block transition metals creating the various chemistry in crystalline porous material. The component of metal in MOFs is considered as the nodes which can be isolated single point or metal cluster and directly linked together by rigid or flexible organic linker units. The organic units (linker or bridging block) which are used to construct MOFs, can be carboxylate commonly or other anions as phosphate, sulfonate, heterocyclic compound rarely. As the key function, the targeted applications need to be considered firstly by choosing the structure of the linker units. Because during the MOFs conformation, the organic linkers could effect to the deprotonation process as well as the linking interaction with metal ions which cause the geometrical structure of MOFs. In addition, the effect of the structure of the coordination environment in MOFs includes the geometry of metal atom used in the synthesis. The simple way to express the most influencing to the topological networks of MOFs is paying attention to the geometry of SBUs. The building blocks of metal cluster are initially formed by the linkages between multi-topic linker such as, 1,4-benzenedicarboxylate (BDC), 1,3,5-benzenetricarboxylate (BTC), biphenyl-3,3',5,5'-tetracarboxylate (BPTA) or 1',2',3',4',5',6'-hexakis(4-carboxyphenyl)-benzene (CPB) and the metal-oxo pieces which are composed in early of reaction process. In 1999, Omar M. Yaghi and co-workers published two archetypical MOFs, MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$, where BDC = 1,4-benzenedicarboxylate) and MOF-199 ($\text{Cu}_3(\text{BTC})_2$, where BTC = 1,3,5-benzenetricarboxylate) which has been reckoned as the benchmark in MOFs chemistry by the first showing the ultrahigh porosity of porous materials. In crystal structure of MOF-5, Zn_4O

plays as model SBU presented by many compounds in MOFs chemistry later (Figure 1).

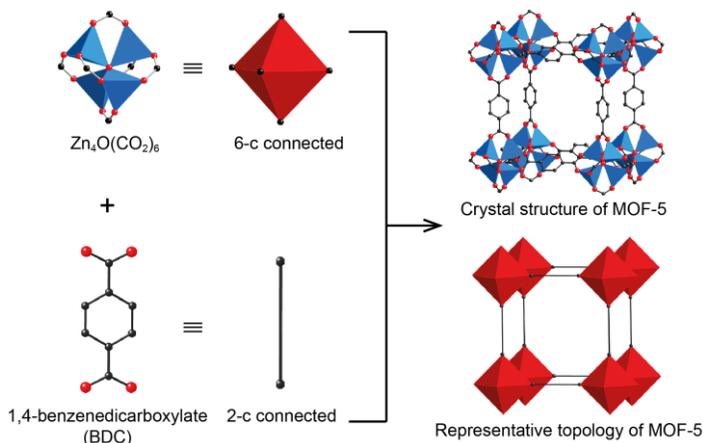


Figure 1. Crystal structure deconstruction for MOF-5 exhibiting clearly 3D extended framework and topological elucidation.

1.3 Interesting features and application of MOFs

MOFs are commonly synthesized by connecting the organic linkers and the metal salts under solvothermal condition by heating at relatively low temperature (lower than 300 °C). The crystal structure of final product, MOFs, can be obtained depend on the characteristics of the linkers such as the geometry, bulkiness, functional groups, rigid or flexible linkages. The role of the MOFs formation is also indicated by the kinds of metal clusters which are used to react with the organic linkers. The mixture of reagents is dissolved in the single solvent or the co-solvent system to adjust the polarity. The important parameters for the synthesis by using solvothermal method are temperature, reagent concentration, the solubility and pH environment under presence of additives or modulators. The reticular chemistry is presented by combination of simplification of linker units and metal cluster representative (point extension) to describe the structural characters of MOFs.

The high porous material in MOFs chemistry was the first reported in 1999 by Yaghi and co-workers, in which the structure was elucidated by single crystal X-ray diffraction, gas sorption at low temperature and low pressure supported the permanent porosity. The forming of the $Zn_4O(CO_2)_6$ octahedral building units which made the chelation to carboxylate linker leads to **fcu** cube topology. The void fraction calculation was found to be 61% with BET surface area $>2300 \text{ m}^2 \text{ g}^{-1}$. The first time one porous material was totally elucidated the crystal structure and other characterizations showing the high porosity compared to traditional porous materials such as activated carbon or zeolites (Figure 2).

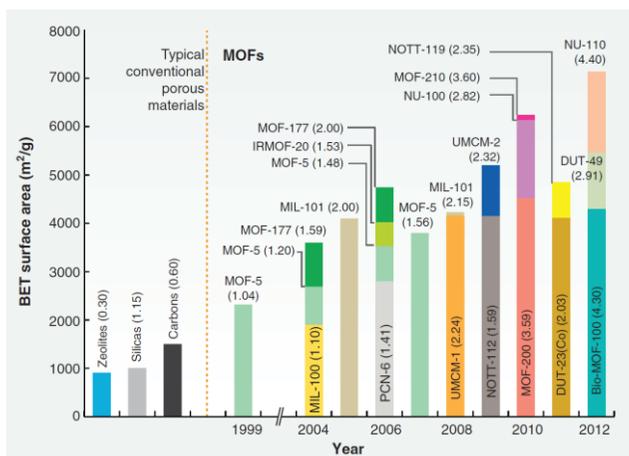


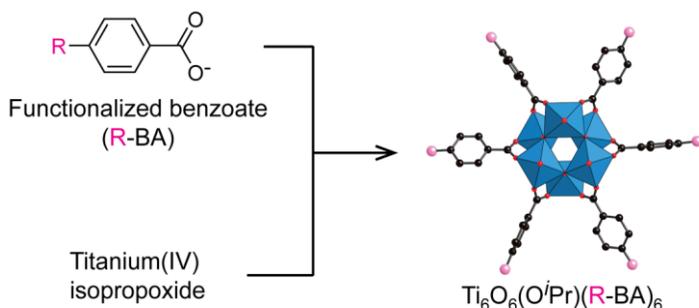
Figure 2. Statistic for surface area of MOFs comparing to conventional porous material.

Studying of gas storage application has been conducted on porous traditional material as activated carbon, zeolites, or carbon nanotubes. MOFs material recently is being received much attention for gas uptake specially hydrogen, carbon dioxide and methane, due to the ultra-high porosity, well-

known structural topology, framework flexibility, tunable pore distribution, leading to the active sites decoration for enhancing the gas affinity.

1.4 Objective

In the chemistry of carboxylate metal–organic frameworks (MOFs), the chelation of the carboxyl organic linker to metal ions gives metal-carboxyl clusters, secondary building units (SBUs), which act as anchors ensuring the overall architectural stability of the MOF. Although many of these SBUs are known as discrete clusters, it has been difficult to directly use them as starting building blocks for MOFs. The main reason is the sensitivity of cluster formation to reaction conditions and, in many cases, the incompatibility of such conditions with those required for MOF synthesis and crystallization. This limitation has prevented access to the vast, diverse, and well-developed cluster chemistry and the potential richness of properties they would provide to MOFs.



Scheme 1. Synthetic scheme depicting the generalized formation of a discrete hexameric Titanium Cluster, which can be appropriately functionalized with amine groups to affect imine Condensation reactions. Atom colors: Ti, blue; C, black; O, red; R groups, pink; H atoms and capping isopropoxide units are omitted for clarity.

In this contribution, we articulate a strategy for making discrete metal clusters in situ that are appropriately functionalized to affect imine-condensation reactions, commonly used in the chemistry of covalent–organic

frameworks (COFs). We find that the chemistry of cluster formation and COFs, when carried out in sequence, overcome the challenge of synthetic incompatibility. Inspired by the chemistry of hexameric titanium oxo clusters, we reasoned that it is possible to functionalize a known cluster with amine functionalized carboxyl ligands (Scheme 1).

Indeed, this allows the resulting cluster to be linked together through imine condensation reactions. Initial synthetic attempts were performed in a sequential, stepwise manner, in which a discrete, isolated Ti(IV) cluster, $[\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{AB})_6]$ (AB = 4-aminobenzoate; O^iPr = isopropoxide), was first synthesized according to previous reports.¹¹⁶ Based on reticular chemistry, this hexagonal building block has six points-of-extension and when linked with a linear linker would lead to an **hxl** layered topology. Thus, titanium(IV) isopropoxide $[\text{Ti}(\text{O}^i\text{Pr})_4]$ and 4-aminobenzoic acid (H-AB) were reacted under solvothermal conditions in isopropanol. After successful synthesis and full characterization of the cluster, exhaustive efforts were undertaken to form the corresponding MOF upon reactions with benzene-1,4-dialdehyde (BDA). However, due to the low solubility of the cluster in a variety of solvents, only poorly crystalline powders or amorphous solids were obtained. Accordingly, a one-pot synthetic approach, with BDA present, was performed given the fact that the synthetic conditions to form the hexameric $[\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{AB})_6]$ were found to be robust.

CHAPTER 2. SYNTHESIS AND CHARACTERIZATION OF MOF-901, -902, -903, -904, AND VNU-18

2.1 Introduction

The synthesis procedure of MOF-901, -902, -903, -904, and VNU-18 was described below. The solvothermal synthesis method was used to synthesize these MOFs. The crystal structure and physical, chemical properties of these MOFs were then fully analyzed.

2.2 Experiment

MOF-901, -902, -903, -904, and VNU-18 were obtained by solvothermal synthesis method. Specially, MOF-901, and MOF-902 need to be synthesized under inert gas and vacuum medium to avoid any effects of water and oxygen. The solvents, which were used in the experiment, are anhydrous.

The obtained materials were full characterized to confirm the crystal structure and the features including power X-ray diffraction (PXRD for MOF-901, -902), single crystal X-ray diffraction (SXRD for MOF-903, -904, and VNU-18), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), microelemental analysis (EA), nitrogen adsorption isotherm at low pressure, 77 K (BET).

2.3 Result and discussion

2.3.1 MOF-901: Synthesis and characterization

- The yield of MOF-901 synthesis is 33.9 % based on titanium isopropoxide.
- Imine linkage in the framework of MOF-901 was proven by Fourier transform infrared spectroscopy (FT-IR).
- The thermogravimetric analysis (TGA) for activated MOF-901 exhibits the thermal stability of MOF-901 up to 200 °C
- The amount of TiO₂ “residue” after burning under airflow matches with the theory of model.

- The linker units were confirmed by nuclear magnetic resonance (NMR). The organic linker containing imine linkage was hydrolyzed by HF 48 % to generate starting reagents: 4-aminobenzoate, and 1,4-benzenedialdehyde which were proven by $^1\text{H-NMR}$.
- The cluster formation is also clarified by nuclear magnetic resonance (NMR) which shows the signal of methoxide caps at 3.15 ppm with the integration of 3 protons.
- The internal surface area of MOF-901 is $550 \text{ m}^2/\text{g}$ based on BET method which strongly agrees with the geometrical area calculated from the ($650 \text{ m}^2/\text{g}$).
- Microelemental analysis for percentage of C, H, N leads to the coincident result between experimental and model structure.
- Crystal structure of MOF-901 was simulated by *Material Studio* v6.0. software.
- Pawley refinement was applied to refine the unit cell parameters of MOF-901.

2.3.2 MOF-902: Synthesis and characterization

- The yield of MOF-901 synthesis is 56 % based on titanium isopropoxide.
- Imine linkage in the framework of MOF-902 was also proven by Fourier transform infrared spectroscopy (FT-IR).
- The thermogravimetric analysis (TGA) for activated MOF-901 exhibits the thermal stability of MOF-902 up to $200 \text{ }^\circ\text{C}$.
- The amount of TiO_2 “residue” after burning under airflow matches with the theory of model.
- The linker units were confirmed by nuclear magnetic resonance (NMR). The organic linker containing imine linkage was hydrolyzed by HF 48 %

to generate starting reagents: 4-aminobenzoate, and 4,4'-biphenyldicarboxaldehyde which were proven by $^1\text{H-NMR}$.

- The cluster formation is also clarified by nuclear magnetic resonance (NMR) which shows the signal of methoxide caps at 3.15 ppm with the integration of ~ 3 protons.
- The internal surface area of MOF-902 is $400 \text{ m}^2/\text{g}$ based on BET method.
- Crystal structure of MOF-902 was simulated by *Material Studio* v6.0. software.
- Pawley refinement was applied to refine the unit cell parameters of MOF-902.

2.3.3 MOF-903: Synthesis and characterization

- The yield of MOF-903 synthesis is 75 % based on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.
- MOF-903 was obtained by large riced shape single crystal
- Azo linkage in the framework of MOF-903 was proven by Fourier transform infrared spectroscopy (FT-IR).
- The thermogravimetric analysis (TGA) for activated MOF-903 exhibits the thermal stability of MOF-903 up to $250 \text{ }^\circ\text{C}$.
- The amount of Fe_3O_4 “residue” after burning under airflow matches with the theory of model.
- Crystal structure of MOF-903 was determined by single crystal X-ray diffraction (SXR).
- Simulated PXRD pattern for MOF-903 is coincident with the experimental PXRD pattern.

2.3.4 MOF-904: Synthesis and characterization

- The yield of MOF-903 synthesis is 75 % based on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.
- MOF-903 was obtained by octahedral shape single crystal.

- The thermogravimetric analysis (TGA) for activated MOF-903 exhibits the thermal stability of MOF-904 up to 270 °C.
- The amount of Fe₃O₄ “residue” after burning under airflow matches with the theory of model.
- The internal surface area of MOF-904 is 1200 m²/g based on BET method which strongly agrees with the geometrical area calculated from the (1500 m²/g).
- Crystal structure of MOF-904 was determined by single crystal X-ray diffraction (SXR).
- Simulated PXRD pattern for MOF-904 is coincident with the experimental PXRD pattern.

2.3.5 VNU-18: Synthesis and characterization

- The yield of VNU-18 synthesis is 75 % based on Cu(NO₃)₂·3H₂O.
- VNU-18 was obtained by light blue single crystal with the needle shape.
- The thermogravimetric analysis (TGA) for activated VNU-18 exhibits the thermal stability of VNU-18 up to 200 °C.
- The amount of CuO “residue” after burning under airflow matches with the theory of model.
- The surface area of VNU-18 was determined by nitrogen adsorption isotherm at low pressure, and 77 K, which shows the value of 1000 m²/g. That value is coincident with the geometry surface area generated from the model structure.
- Crystal structure of VNU-18 was determined by single crystal X-ray diffraction (SXR).
- Topology of VNU-18 was analyzed by *TOPOS* 4.0 package

- Simulated PXRD pattern for VNU-18 is coincident with the experimental PXRD pattern.

2.4 Conclusion

The following MOFs: MOF-901 to MOF-904 and VNU-18 were synthesized and full characterized to elucidate the crystal structure and the properties by model analyses including power X-ray diffraction (PXRD for MOF-901, -902), single crystal X-ray diffraction (SXRD for MOF-903, -904, and VNU-18), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), microelemental analysis (EA), nitrogen adsorption isotherm at low pressure, 77 K (BET).

CHAPTER 3. THE PHOTOCATALYSIS APPLICATION OF MOF-901 AND MOF-902 FOR POLYMERIZATION REACTION UNDER VISISBLE LIGHT

3.1 Introduction

In this chapter, MOF-901, and MOF-902's photocatalysis property was studied by the analyses of UV-Vis spectroscopy, photoluminescence (PL), and Mott-Schottky. The polymerization reaction of methylmethacrylate (MMA) was executed by the promotion of MOF-901 and MOF-902. The results show that MOF-901, -902 can promote this reaction under visible light. The molecular weight of polyMMA products which produced by MOF-901 and MOF-902, are higher than polyMMA product using commercial catalyst P25-TiO₂. In addition, MOF-901, -902 can be used during three consecutive cycle without any lost of performance.

3.2 Experimental

Photocatalysis properties of MOF-901, -902 were studied.

MOF-901 was applied to be a catalyst for the polymerization reaction of MMA under visible light.

MOF-902 was also applied to be a catalyst for the polymerization reaction of MMA as well as other monomers such as BMA, and St under visible light.

These factors affect to the polymerization reaction had been studied: reaction time, amount of co-initiator.

Polymer products were analyzed by GPC analysis to determine the average molecular weight (M_n), and polydispersity index (PDI) and compare to the product which produced by commercial catalyst P25-TiO₂ or other MOFs containing the similar total band-gap energy.

The yield of polymerization reaction was calculated to compare with other catalysts.

3.3 Results and discussion

3.3.1 Photocatalysis properties of MOF-901, and MOF-902

Band gap energy of MOF-901 was calculated based on the UV-Vis spectroscopy and Tauc plot. The value of band gap energy for MOF-901, -902 is 2.65 eV, and 2.50 eV respectively.

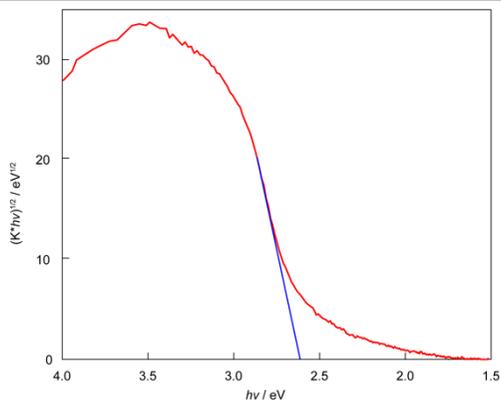


Figure 3. Tauc plot displaying the band gap of MOF-901.

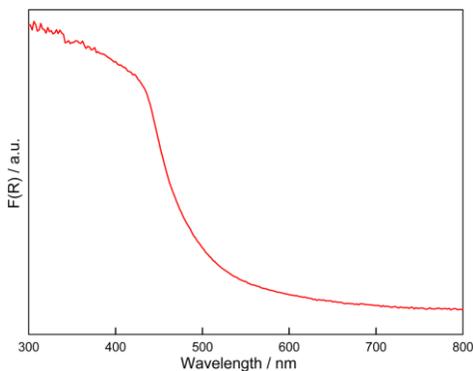


Figure 4. UV-Vis spectroscopy of activated MOF-902.

E_{fb} of MOF-901 was generated by Mott-Schottky analysis. The value is about 0.57 V vs Ag/AgNO₃.

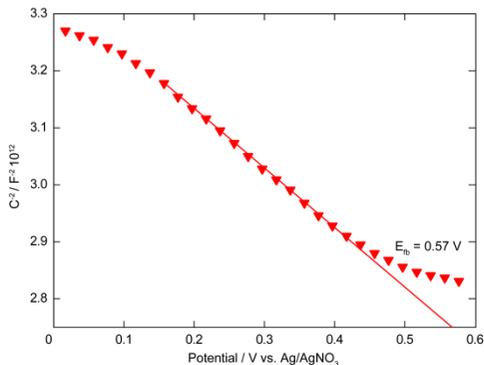


Figure 5. Mott-Schottky plot of MOF-901 at 500 Hz.

3.3.2 Application of MOF-901 for polymerization reaction of methylmethacrylate (MMA)

We used MOF-901 as a photocatalyst in the visible light mediated radical polymerization of methyl methacrylate (MMA) with a co-initiator, ethyl α -bromophenylacetate. Initially, we focused on optimizing the catalyst loading, co-initiator quantity, and reaction time. As shown in Table 1, a catalyst and co-initiator loading of 0.034 mol% and 0.61 mol% (with respect to MMA), respectively, and a reaction time of 18 h was found to be ideal. The optimized conditions resulted in polymerization with a high molecular weight of polyMMA (26,850 g mol⁻¹), high yield (87%), and reasonable distribution, as indicated by a low polydispersity index (PDI) of 1.6. Control experiments were subsequently performed in order to assess the photocatalytic activity of MOF-901. As expected, there was no observable product when the discrete [Ti₆O₆(O^{*i*}Pr)₆(AB)₆] cluster was used, nor in the absence of catalyst (i.e. blank sample) or visible light.

Table 1. Photocatalyzed polymerization of methyl methacrylate (MMA) under visible light irradiation.

Entry	Catalyst [mol%]	Yield [%]	M_n [g mol ⁻¹]	M_w/M_n
MOF-901 ^a	0.034	87	26,850	1.6
P-25 TiO ₂ ^a	0.034	52	17,000	1.6
[Ti ₆ O ₆ (O ⁱ Pr) ₆ (AB) ₆] ^a	0.034	n.d.	n.a.	n.a.
MOF-901 ^b	0.034	n.d.	n.a.	n.a.
Blank ^c	0	n.d.	n.a.	n.a.
MIL-125-NH ₂ ^a	0.034	n.d.	n.a.	n.a.
VNU-1 ^a	0.034	n.d.	n.a.	n.a.

^aReaction conditions: MMA (2.0 M in *N,N*-dimethylformamide), catalyst (0.034 mol%), and ethyl-*o*-bromophenylacetate (0.61 mol%) at room temperature with visible light from a compact fluorescent light bulb (4U, 55 W) for 18 h. ^bReaction performed in the absence of light irradiation. ^cReaction performed without catalyst. n.d. = not detected; n.a. = not applicable; M_n = number average molar mass; M_w = mass average molar mass.

The heterogeneous nature of MOF-901 was validated through recycling experiments. PXRD analysis of this regenerated material revealed that the structure of MOF-901 was maintained. The photoinitiated polymerization reaction was then performed again under identical conditions. The activity of MOF-901 remained, without any loss of performance, over at least three consecutive cycles (Figure 6, 7). Indeed, this recyclability further demonstrates the outperformance of MOF-901 versus other photocatalysts for this purpose.

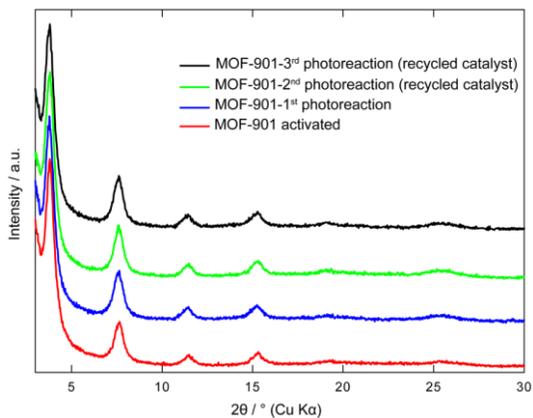


Figure 6. PXRD analysis of MOF-901 showed that the crystalline nature was retained after applying MOF-901 to three consecutive recycles of photoreaction.

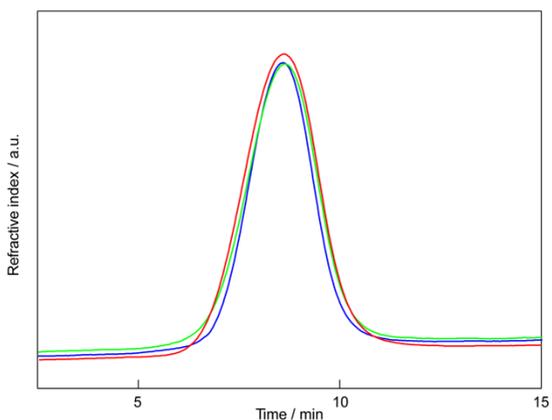


Figure 7. GPC profiles of polyMMA product demonstrated the recyclability of MOF-901 over three consecutive cycles, in which the first (red), the second (blue), and the third photoreactions (green) are shown.

3.3.3 Application of MOF-902 for polymerization reaction of methylmethacrylate (MMA), benzylmethacrylate (BMA), and styrene (St)

The photoactivity of MOF-902 was demonstrated by performing the polymerization reaction of methylmethacrylate (MMA) under visible light in the presence of MOF-902 as an efficient heterogeneous photocatalyst and co-initiator of ethyl α -bromophenylacetate. We reported that MOF-901 could promote to catalyze the polymerization reaction of MMA resulting the high molecular weight of polyMMA ($26,850 \text{ g mol}^{-1}$) and low polydispersity index (1.6). Interestingly, we found that the polydispersity index of polyMMA could be decreased dramatically when using MOF-902 to promote the reaction under coincident synthetic condition. As shown in Table 2, MOF-902 catalyst results the polyMMA with a high molecular weight ($21,470 \text{ g mol}^{-1}$), reasonable yield (50%), and uniform distribution indicated by very low polydispersity index of 1.22, which clearly outperforms the commercial catalyst P25-TiO₂ as well as compared MOFs whose band gap energies are slightly similar to MOF-902 (Table 2).

In order to further investigate the visible light photoresponsive properties of MOF-902 which is hypothesized to affect to the photocatalytic results, we carried out the polymerization reaction with other monomers such as benzylmethacrylate (BMA) and styrene (St). In addition, the organic solvents effect was also studied by carrying out the polymerization reaction under coincident synthetic procedure with changing the reacted solvent. Table 3 depicts that MOF-902 acts as the efficient photocatalyst to promote the reaction to polymerize MMA, BMA with different kinds of organic solvents such as: *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), or 1,4-dioxane. Interestingly, MOF-902 produced the polyMMA and polyBMA with high molecular weight ($22,330 \text{ g mol}^{-1}$ and $32,050 \text{ g mol}^{-1}$, respectively) and low polydispersity index (1.19 and 1.11, respectively). Significantly, MOF-902 promotes the process of photocatalytic reaction leading to produce polymer products of polyMMA and polyBMA in common organic solvents (DMF, THF,

and dioxane) which outperforms MOF-901. It is note that MOF-902 is also more profitable than MOF-901 due to its photoactivity acting as the key factor to result polySt in THF solvent with molecular weight of 6,660 g mol⁻¹ and reasonable distribution presented by polydispersity index of 1.65.

Table 2. Polymerization reaction of methylmethacrylate under visible light in the presence of diverse photocatalysts

Entry	Catalyst (mol%)	Yield (%)	M_n (g mol ⁻¹)	M_w/M_n
MOF-902 ^a	0.034	50	21,470	1.22
MOF-901 ^{a,b}	0.034	87	26,850	1.60
MOF-902 ^c	0	n.d.	n.a.	n.a.
MOF-901 ^c	0	n.d.	n.a.	n.a.
P25-TiO ₂ ^{a,b}	0.034	52	17,000	1.62
UiO-66 ^a	0.034	n.d.	n.a.	n.a.
UiO-66-NH ₂ ^{a,b}	0.034	13	18,500	1.61
VNU-1 ^a	0.034	n.d.	n.a.	n.a.
MIL-125 ^a	0.034	n.d.	n.a.	n.a.
MIL-125-NH ₂ ^{a,b}	0.034	n.d.	n.a.	n.a.

^aReaction condition: MMA (2.0 M in *N,N*-dimethylformamide), catalyst (0.034 mol%), and ethyl α -bromophenylacetate (0.61 mol%) at room temperature with visible light from a compact fluorescent light bulb (4U, 55 W) for 18 h. ^bThe GPC result was used from MOF-901 experiment; polyMMA product was also reproduced to confirm the previous results. ^cReaction performed without catalyst. n.d. = not detected (or trace which cannot be isolated); n.a. = not applicable; M_n = number average molar mass; M_w = mass average molar mass.

Table 3. Studies of MOF-902 catalysis property with various monomers in comparison to MOF-901

Monomer ^a	Solvent	Catalyst	Yield (%)	M_n (g mol ⁻¹)	M_w/M_n
MMA	DMF	MOF-901 ^b	87	26,850	1.60
		MOF-902	50	21,470	1.22
	THF	MOF-901	n.d.	n.a	n.a.
		MOF-902	45	21,700	1.24
	Dioxane	MOF-901	n.d.	n.a	n.a.
		MOF-902	28	22,330	1.19
BMA	DMF	MOF-901	n.d.	n.a	n.a.
		MOF-902	80	27,800	1.16
	THF	MOF-901	39	29,778	1.14
		MOF-902	95	23,434	1.10
	Dioxane	MOF-901	n.d.	n.a	n.a.
		MOF-902	71	32,050	1.11
St	DMF	MOF-901	n.d.	n.a	n.a.
		MOF-902	n.d.	n.a	n.a.
	THF	MOF-901	n.d.	n.a	n.a.
		MOF-902	13	6,660	1.65
	Dioxane	MOF-901	n.d.	n.a	n.a.
		MOF-902	n.d.	n.a	n.a.

^aReaction conditions: Monomer (2.0 M in organic solvent), catalyst (0.034 mol%) ethyl α -bromophenylacetate (0.61 mol%) at room temperature with visible light from a compact fluorescent light bulb (4U, 55 W) for 18 h. ^bThe GPC result was used from MOF-901 experiment; polyMMA was also reproduced to confirm the previous results.

3.4 Conclusion

In conclusion, we have reported the synthesis of MOF-902 constructed from a hexameric titanium $\text{Ti}_6\text{O}_6(\text{OMe})_6(\text{AB})_6$ which is formed by in situ generation and 4,4'-biphenyldicarboxaldehyde (BPDA). The crystal structure of MOF-902 was analyzed by powder XRD and supported analyses. By incorporating the high conjugated imine linking unit, MOF-902 absorbs the visible light at red-shift region leading to low band gap energy (ca. 2.50 eV). The visible light responsive activity of MOF-902 was confirmed by the photocatalytic properties enhancement. MOF-902 exhibited high performance in photocatalysis application of polymerization reaction with various monomers such as MMA, BMA, and St, resulting in high molecular weight (M_n) and low PDI of polymer products.

CHAPTER 4. CONCLUSION AND SCIENTIFIC CONTRIBUTION

In conclusion, we have successfully synthesized and full characterized Titanium–Organic Framework-901 (MOF-901) based the combination of in situ cluster formation and Covalent Organic Frameworks chemistry. The crystal structural analysis of MOF-901 was studied by powder X-ray diffraction and other analysis methods, which supported the understanding of crystal structure and features of the material. MOF-901 displayed the high performance of photocatalysis properties promoting the polymerization reaction of methyl methacrylate (MMA) under visible irradiation at room temperature. The molecular weight of polyMMA product is larger than the polyMMA product produced by other catalyst including UiO-66-NH₂, MIL-125-NH₂, VNU-1, and P25-TiO₂. Moreover, the polyMMA product was found to be more uniform than the product resulted by compared catalysts, which was exhibited by 1.6 in calculated of polydispersity index (PDI). The recyclability property of MOF-901 also reveals by three consecutive cycles investigation without any loss of performance.

In addition, MOF-902, which is isoreticular to MOF-901 was successfully synthesized by applying the similar approach and procedure in MOF-901 synthetic scheme. MOF-902 was also fully characterized including powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible spectroscopy (UV-Vis), nuclear magnetic resonance (NMR), elemental analysis (EA). The crystal structure of MOF-902 was modelled and generated the pore size in calculated of 16 Å. The internal surface area of MOF-902 is lower than MOF-901 due to the low crystallinity or defect sites which is common in MOFs/COFs material. MOF-902 performs the better photocatalysis properties than MOF-901 in promotion of polymerization reaction of MMA and other monomers such as BMA, and St. The molecular weight of polymer products which were produced by MOF-902, is as high as the product produced by MOF-901. However, the

polymer products resulted from MOF-902 catalyst are more uniform than MOF-901 showing by the lower PDI value of 1.2 vs 1.6.

In term of scientific contribution, we absolutely afforded the novel approach to synthesize MOFs material based on Ti-oxo cluster which is rare in MOFs chemistry. The synthetic scheme was provided to prove the *in situ* formation of Ti-oxo cluster during the robust synthesis. The work was also contributed to MOFs chemistry the route which can overcome the challenges for the synthesis of MOFs based Ti-oxo cluster which normally occur as sol, gel, or amorphous solid. The development of new, crystalline, and extended structures, most notably based on Ti(IV), has been of great interest to the community of materials scientists owing to the difficulty in realizing such materials (total of 5 Ti-based MOFs are known, compared to thousands of other metal ions). There remains an absence of a universal approach for achieving new Ti-MOFs.

Furthermore, we presented the synthesis scheme to produce another three novel MOFs containing Fe(III) (MOF-903, -904) and Cu(II) (VNU-18) which are fully characterized the crystal structure and chemical features. These MOFs might be contributed to enrich the crystal structure database of porous materials and ordered crystalline-based materials.

Viet Nam National University – Ho Chi Minh City

University of Technology

HA LAC NGUYEN

**DESIGNED SYNTHESIS OF NOVEL METAL–ORGANIC
FRAMEWORKS FOR PHOTOCATALYST APPLICATION**

Doctorate Thesis – Summary

Publications

1. **H. L. Nguyen**, F. Gándara, H. Furukawa, T. L. H. Doan, K. E. Cordova, O. M. Yaghi, A Titanium-Organic Framework as an Exemplar of Combining the Chemistry of Metal- and Covalent-Organic Frameworks, *J. Am. Chem. Soc.* **2016**, *138*, 4330 (**IF = 13.038**)
2. **H. L. Nguyen**, T. T. Vu, D. Le, T. L. H. Doan, V. Q. Nguyen, N. T. S. Phan *ACS Catal.* **2017**, *7*, 338 (**IF = 9.307**)

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